[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

ALCOHOLYSIS OF TRIARYLBORANES

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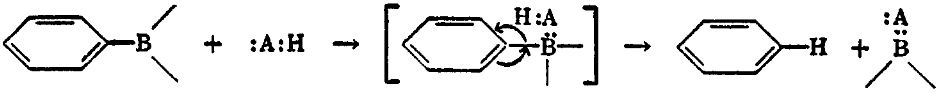
Diarylborinic acids and their derivatives are relatively unfamiliar compounds. The literature on their preparation and properties is sparse, and the products have been inadequately characterized (1–3). Attempts to repeat some of the published directions were unsuccessful, as were attempts to modify well-known procedures for preparation of arylboronic acids and triarylboranes (4, 5). Accordingly, we investigated the cleavage of triphenyl- and tri-α-naphthyl-borane by certain acidic reagents.

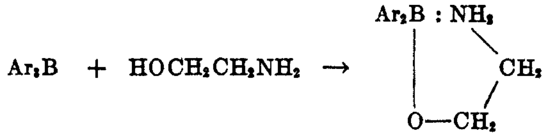
Cleavage of trialkylboranes by hydrogen chloride or bromide can be stopped cleanly at the dialkylboron halide stage by control of the temperature (6, 7). In several attempts, however, the attack of hydrogen bromide upon tri-α-naphthylborane went beyond cleavage of a single naphthyl group; the results with acetic acid were no better. Methyl borate was formed in the reaction of methanol with tri-α-naphthylborane before all of the borane had gone into solution. With triphenylborane and purified methanol, it was possible to isolate (as the ammonia complex) a small amount of methyl diphenylborinate; however, with ordinary reagent methanol, the major product was phenyl diphenylborinate resulting from oxidation by trace impurities, possibly oxygen or formic acid.

$$Ph_3B + CH_3OH \rightarrow Ph_2BOCH_3$$

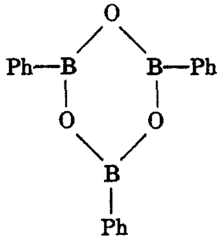
Methanolysis of triarylboranes did not appear to be a promising general route to methyl diarylborinates. Replacement of one aryl group by alkoxyl would reduce steric hindrance at the boron atom and further attack by methanol should be more rapid. Electron release by the groups attached to boron is an even more important factor. Alkyl groups are only weakly electron-releasing, phenyl and α-naphthyl much more so. The introduction of an electron-attracting group (halogen, alkoxyl, acetoxyl) onto the boron atom should retard cleavage of a second alkyl or aryl group. This factor is doubtless responsible for the success in preventing further cleavage of dialkylboron halides (6, 7). With arylboranes, however this retardation seems completely overshadowed by powerful electron release from the aryl group (particularly naphthyl) in the transition state. Additional examples are found in the work on cleavage of arylboronic acids (8, 9).

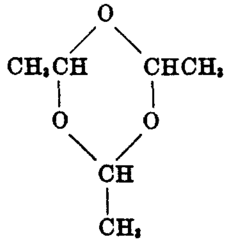


Some external reagent might stop the cleavage at the desired point. For example, a hindered base might possess such steric requirements that it could not coordinate with a triarylborane but could complex with a diarylborinic acid derivative. 2,6-Lutidine and 2,4-lutidine were ineffective in stopping the reaction of tri-α-naphthylborane with methanol at the dinaphthylborinate stage. The solution was finally found in chelation; β-aminoethyl di-α-naphthylborinate and β-aminoethyl diphenylborinate could be obtained simply by refluxing the triarylborane with ethanolamine in benzene solution. The cleavage appeared to be slower with triphenylborane, as predicted in terms of electron release. Diethylethanolamine was ineffective, and a mixture of products was obtained from tri-α-naphthylborane; models showed that β-dimethylaminoethyl di-α-naphthylborinate could not close the chelate ring.[1]



Structural analogy suggested that 2,4,6-triphenylboroxene (the cyclic trimer of PhB=O) might react with Grignard reagents as does paraldehyde. The former reacted with one mole of phenylmagnesium bromide to form a complex whose ether solution gave a negative Gilman test for Grignard reagent; on addition of water, benzene and triphenylboroxene were recovered.[2] Further amounts of Grignard reagent produced triphenylborane, but diphenylborinic acid could not be isolated.[3]





The reaction of boron fluoride with several different mole ratios of phenylmagnesium bromide led to isolation of triphenylborane or benzeneboronic acid (4, 5), but not diphenylborinic acid.[3] α-Naphthylmagnesium bromide behaved similarly. It is curious that the reaction of boron chloride with α-naphthylmagnesium bromide stopped with the production of α-naphthylboron dichloride; further reaction could not be induced even in boiling benzene (14). Forcing the reaction by use of α-naphthyllithium in boiling benzene led to a tarry mixture.[4]

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[1] Letsinger, private discussion, noted that the less hindered β-diethylaminoethyl diphenylborinate could be prepared.

[2] This is not an uncommon behavior of Grignard reagents. *Cf.* the reaction of benzophenone with phenylmagnesium bromide (10, 11). See also (12).

[3] Possibly the addition of ethanolamine during the work-up would have permitted its isolation.

[4] The reaction of Grignard reagents upon borate esters (2) was unsuccessful in our hands. Recently Letsinger, in a Communication to the Editor (13), observed that diarylborinic acids could be isolated from this reaction as their β-aminoethyl esters; the properties of his products are similar to ours.

EXPERIMENTAL

Tri-α-naphthylborane and ethanolamine. A mixture of 7.15 g. (0.015 mole) of tri-α-naphthylborane [containing one mole of benzene of crystallization (15)], 2.8 g. (0.045 mole) of freshly distilled dry ethanolamine, and 100 ml. of dry benzene was refluxed for 4½ hours. The precipitate which formed (3.16 g., 64%, m.p. 197° dec.) was collected. Naphthalene was isolated from the filtrate. The β-aminoethyl di-α-naphthylborinate was crystallized from benzene five times for analysis; m.p. 205° dec. (evacuated capillary).

Anal.[5] Calc'd for $C_{22}H_{20}BNO$: C, 81.29; H, 6.47; N, 4.30.
Found: C, 80.87; H, 6.44; N, 4.28.

Triphenylborane and ethanolamine. The above procedure was followed, except that the mixture was refluxed for 12 hours under nitrogen. The yield of β-aminoethyl diphenylborinate, m.p. 188–190° dec. after one crystallization, was 68%.

Anal. Calc'd for $C_{14}H_{16}BNO$: C, 74.70; H, 7.16; N, 6.23.
Found: C, 74.88; H, 7.02; N, 6.44.

Tri-α-naphthylborane and methanol. A sample of tri-α-naphthylborane (2.0 g.) dissolved on refluxing for ½ hour with 100 ml. of methanol. The methanol removed by distillation contained methyl borate (green flame), and the residue consisted of naphthalene and unreacted tri-α-naphthylborane. Similar results were obtained with lesser amounts of methanol in a benzene solvent and also with ethanol under both conditions.

Triphenylborane and methanol. A solution of 10.8 g. of triphenylborane in 100 ml. of methanol was refluxed for 137 hours. In this and subsequent operations involving triphenylborane, a nitrogen atmosphere was maintained. The methanol was removed and the deep red residue was distilled; 3 ml., b.p. 55–165°, and 5.5 ml., b.p. 168–171°, were collected at 2.2 mm. The latter fraction, a viscous, highly refractive oil, crystallized when chilled in liquid air and stored in a refrigerator for a day, the process being repeated three times. A sample of the solid was dissolved in 60–75° petroleum ether and the solution was saturated with dry ammonia. The precipitate was recrystallized twice from benzene-petroleum ether, m.p. 152–153°.

Anal. Calc'd for $C_{18}H_{18}BNO$: C, 78.57; H, 6.59; N, 5.09.
Found: C, 78.79; H, 6.55; N, 5.02.

A sample of the original solid, on standing with water, formed phenol which was identified as tribromophenol. From this result and the analytical data, the product appears to be phenyl diphenylborinate. In view of the care taken to exclude oxygen, it appears to have been formed from some impurity in the methanol, probably formic acid.

In a similar experiment, 1.0 ± 0.2 mole of benzene was liberated, as determined by the refractive index of the methanolic distillate. The residue, dissolved in carbon tetrachloride, was allowed to stand with water for two weeks. Phenol was isolated and identified as before; the organic layer yielded 34% of triphenylboroxene, m.p. 214–216°.

In a third experiment in which particular care was taken to use pure solvents and to exclude oxygen, the residue after removal of methanol was dissolved in petroleum ether and precipitated with ammonia. The ammonia complex was reprecipitated from petroleum ether with ammonia, then recrystallized from methyl ether-ammonia; it had no definite melting point. Analysis was consistent with methyl diphenylborinate-ammonia somewhat contaminated by triphenylboroxene or methyl benzeneboronate.

Anal. Calc'd for $C_{13}H_{16}BNO$: C, 73.2; H, 7.6; N, 6.6.
Found: C, 72.28; H, 7.41; N, 6.65.

In connection with this work, it was noted that silicic acid in a chromatographic column under nitrogen pressure caused cleavage of aryl-boron bonds.

Cleavage of tri-α-naphthylborane by acids. Acetic acid under various conditions of time and temperature converted tri-α-naphthylborane to mixtures of triacetoxyborane, naphthalene, and unreacted starting material. Anhydrous hydrogen bromide in boiling benzene for 45 minutes, followed by cold water, converted 2 g. of tri-α-naphthylborane into 0.95 g. of

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[5] Microanlyses by Goji Kodama and Anna Griffin, University of Michigan.

naphthalene, 0.54 g. of unreacted starting material, and 0.46 g. of crude (0.30 g. purified) α-naphthaleneboronic acid. Results at lower temperatures were similar.

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SUMMARY

Triphenyl- and tri-α-naphthyl-borane react with ethanolamine to form aminoethyl diarylborinates. These esters are stable to further alcoholysis, probably because of chelation. Methanolysis was much less readily controlled. Cleavage is discussed in terms of electron-release in the transiton state.

Other methods from the literature for the synthesis of diarylboronic acid derivatives were found to be inferior.

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